PULSED LASER ABLATION OF CU2ZNSNS4

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Introduction

Cu_2ZnSnS_4 (CZTS) is regarded as the best candidate to replace $CuIn_xGa_{(1-x)}Se_2$ (CIGS) and CdTe photovoltaic because it is nontoxic and abundant, thus lower in cost [1, 2]. CZTS formed in the structure of stannite and kesterites, with a direct bandgap of 1.38 to 1.5 eV and absorption coefficient of > 10^4 cm^{-1}, making it suitable for thin film solar cell. The Shockley–Queisser limit of a single junction CZTS cell is calculated to be ~ 31.5%. Experimentally, CZTS as thin film absorber has been tested in solar cell, and the efficiency has increased very rapidly over the years from 0.66% in 1996 to 11.5%, reported by IBM in August 2012 [3]. It is also envisaged that CZTS, together with CuZnSnSe with a bandgap of ~0.9, can be fabricated into tandem cell for even higher efficiency.

CZTS thin films can be deposited by various chemical and physical methods such as photochemical process, sol-gel, sputtering, co-evaporation and also pulsed laser deposition [1, 4]. However, problems such as non-ideal composition and unwanted secondary phases affect the performance of the solar cell. Pulsed laser deposition is versatile and has the advantage of retaining the stoichiometry of complex materials such as superconducting oxides. A comparison of CZTS films deposited by sputtering and PLD shown that PLD to be better in preserving the stoichiometric of the materials, and hence less defects and better crystallinity [5]. Another recent report shows that single kesterite crystal structure without any other secondary phases was formed by using PLD [6].

In this work, CZTS films were deposited by using pulsed Nd:YAG laser ablation of a quaternary Cu_2ZnSnS_4 target. The films were grown at room temperature onto glass and silicon substrates. The dependent of the properties of the films: morphology, composition, optical properties are studied and discussed with respect to laser parameters.

Experimental

A Nd-YAG laser (third harmonic, 355 nm, 4.7 ns) (EKSPLA, NL301) was used for ablation at a repetitive-rate of 10 Hz. The deposition was performed at 10^{-6} Torr from a Cu_2ZnSnS_4 target (99.99% purity, Super conductor materials, Inc.). Corning glass and Si wafer were used as the substrates and they were ultrasonically cleaned prior to use. The laser beam was focused to a size of ~1 mm x 0.9 mm which resulted in laser fluence of 0.5 to 4 J/cm^2. The laser beam rastered an area of 6 x 6 mm^2 on the target surface and the target-substrate distance was kept at 5 cm. Deposition were carried out for 45 minutes. The films were not annealed after growth.

The films thicknesses were measured by using a stylus profilometer. The films properties were characterized by using UV–vis–NIR spectrophotometer (AvaLight-DHc and Oceanoptics S2000), atomic force microscopy (Nanosurf) and scanning electron microscope with energy dispersive xray (Hitachi).

Results and discussions

Nanostructured CZTS films were deposited on glass and Si substrates. CZTS films deposited at 2 Jcm^{-2} is shown in the Figure 1.

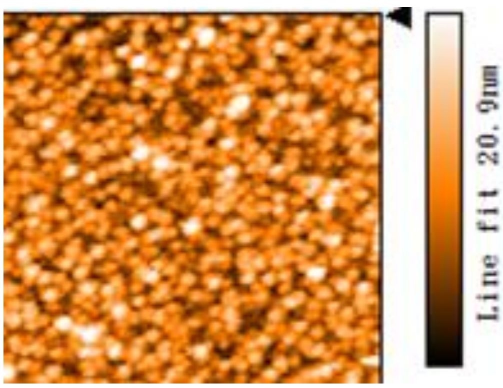

Fig. 1 AFM image of CZTS films deposited at 2 Jcm^{-2} (1 μm × 1 μm).

The lateral size of the nanostructures were ~ 50 nm. The growth rate increases from 0.019 nm/pulse to 0.14 nm/pulse as laser fluences increased from 0.5 to 4 Jcm^{-2}. The thicknesses of the films were shown in Table 1.

Table 1 Properties of CZTS films deposited at 0.5- 4 Jcm^{-2}.

Laser Fluence (Jcm^{-2})	Thickness (nm)	Optical Bandgap (eV)
0.5	50	3.1
1	80	2.9
2	150	1.9
4	375	2.3

The highest absorption coefficient of the films was obtained from deposition at 2 Jcm^{-2} (Figure 2). The optical bandgap, E_g is deduced from a Tauc plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ based on the relationship:

$$\alpha h\upsilon = A(h\upsilon - E_g)^m$$

where A is constant, m is ½ for direct transition. The optical properties of the films are summarized in Table 1.

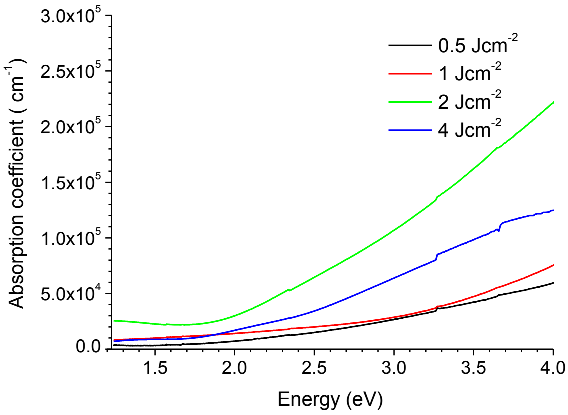

Fig. 2 Transmittance of CZTS films deposited at 0.5- 4 Jcm^{-2}.

XRD show that the as-deposited films are amorphous for deposition at 0.5, 1 and 4 Jcm^{-2}, but a small peak attributed for (200), (004) was obtained for the sample deposited at 2 Jcm^{-2} (Fig. 3). Compositional analysis by EDX indicated that only CZTS films deposited at 2 Jcm^{-2} has close stoichiometry with the desired ratio of Cu: Zn: Sn: S of 2:1:1:4. The values obtained were 2.1: 1.0 : 1.2: 3.3. This give rise to a Cu/(Zn+Sn) ratio of 0.96.

The results show that deposition at room temperature by 355 nm laser can lead to near stoichiometry films at a narrow range of laser fluence. At lower or higher laser fluence, the ablation efficiency of each element is affected, and results in variations in the composition of the films. However, post growth annealing will be required to improve the crystallinity of films.

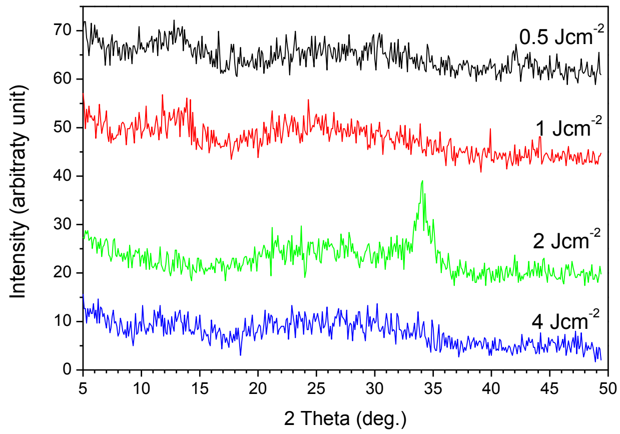

Fig. 3 XRD of CZTS films deposited at 0.5- 4 Jcm^{-2}.

Conclusion

In this work, nanostructured CZTS films were grown at room temperature by using 355 nm laser. The properties of the films depend crucially on the laser fluence. The best films were obtained at laser fluence of 2 Jcm^{-2} where the absorption coefficient was > 10^4 cm^{-1}, and the derived optical bandgap is ~1.9 eV.

Acknowledgments

We acknowledge the support from Telekom Malaysia RDTC/130823, Multimedia University and University Malaya, Malaysia.

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